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Proximal soil nutrient sensing using electrochemical sensors

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Abstract

Conventional soil sampling and laboratory analysis is time consuming and expensive. It does not provide information at the spatial or temporal resolution required for applications such as precision agriculture (PA). The development of proximal soil sensors is important for improving our understanding of soil variability. In terms of PA, they may improve the efficiency of crop production. Proximal soil sensors should provide repeatable measurements; should be rapid, inexpensive and robust. A number of on-the-go proximal soil sensors have been developed and are commercially available. Currently, there are no proximal soil sensors that measure soil nutrient concentration directly. Their development is important. This paper reviews work towards the development of proximal soil nutrient sensors using two forms of electrochemical sensors: Ion Selective Electrodes (ISEs) and Ion Sensitive Field-Effect Transistors (ISFETs). However, both technologies have limitations. This paper will address some of these issues and outline our current work towards the development of a Multi Ion Measuring System (MIMMS). Our preliminary results suggest that by characterising the chemistry of the system and using a novel system design it may be possible to provide the response time, accuracy and robustness required for on-the-go proximal soil nutrient sensing.

Keywords: Proximal Soil Sensing; Ion Selective Electrodes; Ion Sensitive Field-Effect Transistors

1. Introduction

The ability to collect high spatial resolution data of soil chemical and physical properties has proven very beneficial for site specific crop management. Current methods typically employ the use of high resolution EMI or soil electrical resistivity measurements combined with high resolution crop yield data to delineate management zones.

There has been a fair amount of work towards the development of proximal soil sensors for on-the-go measurement of soil nutrients and pH. Adsett et al. (1999) developed a system for on-the-go measurements of soil nitrate using an automated soil collection system that comprised a soil metering and delivery system. Nitrate was extracted using deionised water and analysed with a nitrate ISE. Laboratory testing showed prediction of nitrate with 95% accuracy in 6 seconds.

Birrell and Hummel (2001) reported the development of a multi-ISFET nitrate sensor using a Flow Injection Analysis (FIA) system. The system was capable of measuring soil nitrate in manually extracted soil solutions ($r^2 > 0.9$) in 1.25 seconds.

While these and other similar studies show that potentially ISEs and ISFETS may be used for proximal sensing, they have obviously had limited success. Currently there is only one commercial on-the-go proximal soil sensor for direct measurements of soi pH (Adamchuk et al. 2006). The Veris pH manager consists of a sample shoe that periodically brings a core of soil into direct physical contact with two pH electrodes while traversing the field. This technique employed by the Veris pH sensor is referred to as Direct Soil Measurements (DSM). DSM was also adapted to the measurement of K^+, Na^+ and NO_3^- on naturally moist soil samples (Adamchuk et al., 2005) and for soluble potassium and residual nitrate. The DSM technique was capable of distinguishing between very low and very high concentration levels.

The DSM approach is the first in a series of techniques being explored. While the primary advantage of this technique lies in its simplicity, it is relatively variable and harsh on the ISEs. An alternative approach has been the use of a batch style processing and chamber based analysis. Viscarra Rossel et al. (2004) developed a chamber based system for on-the-go measurement of soil pH, and estimations of Lime Requirement (LR). The system conducted automated soil collection, sieving to a size fraction of < 2mm, measuring of a known volume of soil, mixing with soil lime requirement buffers and measuring with a pH ISFET. The technique relied on the characterization of the kinetics of the chemical reactions for rapid predictions of the reaction equilibriums (Viscarra Rossel and McBratney, 2003).

Using a similar approach, Sethuramasamyraja et al. (2008) explored the use of a chamber based measurement system which was referred to as an Integrated Agitation Chamber Module (IACM). ISEs selective for H^+, NO_3^- and K^+ are immersed in the soil extract solution, providing an environment more physically suitable to ISEs. They also observed the effects of various soil:water ratios, rinsing and extraction water quality, agitation and the requirement for Ionic Strength Adjustment (ISA). It was reported that the best parameters for this system are agitated purified water extraction, a fixed soil:water ratio of 1:1, regular tap water for electrode rinsing and no ISA was necessary. However, in this work there was no characterisation of the chemical reactions.

Most of these studies tend to focus on restraints imposed by field operation, but there has been little work identifying and solving some of the fundamental issues associated with these measurements. There has also been little published work characterising the chemistry of the systems, and the effect of variable conditions such as soil moisture and temperature.

Additionally, work to date has inherently been limited to soluble or plant available ion concentrations. Information on both soluble and exchangeable components is important in management decisions due to the buffering nature of the soil, for example in the measurement of LR and fertiliser application.

This paper will review some recent developments and research into both ISEs and ISFETs for on-the-go sensing. It also briefly outlines the characteristics and limitations of the sensors and introduces some preliminary work towards the development of a multi-ion measurement system (MIMS) that may be use for on-the-go proximal sensing.

2. Ion Selective Electrodes

Ion selective electrodes are potentiometric sensors. The voltage potential at the glass membrane surface is related to the target ion concentration in the measurement solution. They are capable of providing direct measurements in unfiltered soil extracts or slurry which make them an attractive option for proximal soil sensing. They are also relatively cheap and require little supporting hardware.

2.1 ISE response time

Ion Selective Electrodes have a slow response time; typically they produce a 90% response in ten seconds or more. The response time is affected by many factors and includes both the electrochemical cell as well as the measurement electronics. This presents difficulties for the implementation of ISEs for proximal sensing. It also presents difficulties when trying to observe initial ion exchange kinetics. If the response time was constant, and the response of the ISE well defined, the implications would be reduced. However this is generally not the case.

2.1 Ion Interference

Ion selective membranes are not perfectly selective to a particular ion and suffer interference from other ionic species present in the analyte. As a result, not all extracting solutions are compatible with ISEs. High concentrations of potentially interfering ions in these solutions reduces the sensitivity of the ISE to the target ion, and in some cases the ISE exhibits no response to changes in target ion concentration. The interfering ions depend on membrane composition, so they differ between ISE types and manufacturers. In developing a MIMS the list of interfering

ions to avoid can preclude almost all traditional extracting solutions. Research has been conducted on identifying a universal extracting solution for multiple ions in an ISE based analysis system (Kim et al. 2007). They found the Kelowna soil extractant to be compatible with specified ISEs for nitrate, potassium and phosphorus. However, this solution is a mixture of various chemicals which may have environmental consequences.

3. Ion Sensitive Field Effect Transistors

Ion Sensitive Field Effect Transistors (ISFETs) and Chemically Modified Field Effect Transistors (CHEMFETs) operate on much the same principle as ISEs, but with the membrane voltage potential acting as the gate source for a Field Effect Transistor (FET). For example, the pH ISFET is a CHEMFET with an H^+ sensitive compound deposited on the gate. The drain-source current flow through the FET is related to the ion concentration in solution. ISFETS offer several advantages over ISEs, being considerably smaller, and offering improved durability, however the primary advantage for PSS is the improved sensor response time. The use of the FET as a current modulator with the appropriate interface circuitry providing a low impedance analog output, offers a far superior signal to noise ratio. They do suffer from higher drift, requiring more frequent calibration and typically have a shorter life time.

Despite being a relatively old technology (Bergveld 2003) there are currently very little if any commercially available ISFET sensors for ions other than H^+. While particularly useful for PSS, drawbacks such as limited life time and biocompatibility restrict their applications to areas such as the biomedical sciences. Similarly, the promise of miniaturised sensors has been hindered by reference electrode requirements (Janata 2004), which helps limit their commercial viability.

4. Variation of ISE and ISFET static and dynamic properties

Variation of ISE and ISFET response such as changes in sensitivity and drift are a major source of error for these systems. ISEs are not considered precision analytical devices and require frequent recalibration to maintain measurement accuracy. While ISFETs suffer from an increased drift and hysteresis over ISEs, the slow response time of ISEs prevent frequent recalibration. The soil extract solution is particularly bad at inducing variation in these properties.

5. Requirements for on-the-go sensing

Three fundamental specifications that must be met by this type of proximal soil sensor are analysis time, measurement precision and cost. For on-the-go sensing, sample acquisition and measurement needs to satisfy the field variability of the target macronutrient at least to a level for practical management. The sensor must also satisfy an economic rationale, in that the cost of the additional information must not exceed the financial and environmental benefits gained. Accuracy requirements for such a sensor are slightly lax, especially when augmenting the data with prior or post information. The primary concern is providing an acceptable precision in order to capture variability. The rational for proximal soil sensing is that although measurements using proximal soil sensors may be less accurate than those obtained by conventional laboratory analyses, data is collected at much higher resolutions and in a less costly and takes less effort to acquire. Viscarra Rossel & Walter (2004) demonstrated this with field measurements of soil pH using an ISFET. They showed that proximal soil pH measurements were 100 times for efficient in terms of the effort required to make the measurements and their cost. Furthermore, the authors showed that the resulting maps more truly depicted the spatial and temporal variation in soil pH.

6. Ion Exchange

Extraction of exchangeable ions is the rate limiting step in these measurements. It is target ion and extracting solution dependant, but can take up to thirty minutes or more to reach equilibrium. Current efforts are limited to the measurement of the soil soluble ion concentration, where the process of extracting ions into the measurement solution or slurry is only limited by ion diffusion processes.

The pH and LR sensor developed by Viscarra Rossel et al. (2004) attempted to solve this problem by modelling the kinetics of the reaction and making predictions of LR. The analytical chamber contained a pH ISFET that was used to observe and model exchange kinetics (Viscarra Rossel and McBratney 2003). Successive observation of exchange kinetics for many soil types was used to develop a prediction method capable of estimating soil pH and LR on-the-go using only initial observations. The authors could estimate LR with an average error of approximately 1 Mg/ha.

A similar approach which models the kinetics of soil reactions is being explored for the development of the MIMS and prediction of ion exchange equilibriums for nitrate, sodium and potassium.

7. Experimental Work

This section briefly outlines hardware development and experimental work currently in progress.

### 7.1 Soil analytical unit & Hardware

The soil analytical unit incorporates a batch style measurement method, with an ISE sensor array for the on-line monitoring of ion exchange kinetics. The unit incorporates automated chamber evacuation and rinsing and sensor calibrations. The sensor array is made up of ISEs selective for nitrate, sodium, potassium and a lithium acetate reference electrode. It also includes a stainless steel temperature probe, providing required bias current return through the sample solution. The ISEs are interfaced to a National Instruments NI-6218 USB data acquisition unit, which also provides control I/O for pneumatic and pump functions. Burr Brown INA116 instrumentation amplifiers are used for impedance conversion. Since the observation of initial exchange kinetics is critical to this work, particular attention has been placed on proper faraday shielding to maximize signal to noise ratio (SNR). Additionally, the ISE cable shielding is 'driven' by the INA116 cable drivers to minimize any cable capacitance and its effect on response time at such high input impedances.

The MIMS is currently under development and it provides a platform to facilitate the observation of ion exchange kinetics for multiple soils, both in the laboratory and ultimately in the field. It is an agitated chamber based system that provides autonomous dispensing of calibration solutions, extracting solutions, agitation and system washout (Figure 1).

7.2 Objectives

The objectives of this experimental work can be summarised as follows.
1. Refine analytical unit parameters such as extracting solution type, soil:solution ratio's and agitation speeds.
2. Observe and characterise nitrate, potassium and sodium ion exchange kinetics for a wide range of soils.
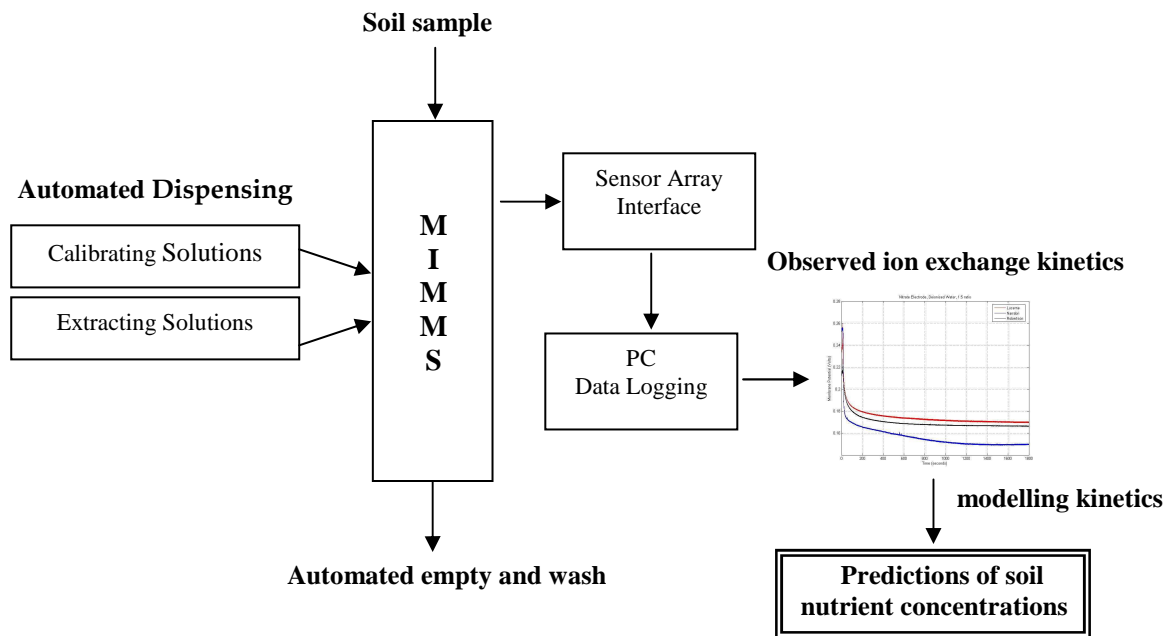
Figure 1. Analytical Unit (MIMS) with measurement and modelling processes

3. Use system modelling techniques to extract signal components corresponding to ISE response, soluble ion concentration and exchangeable ion concentration.

4. Quantify the effects of variation in ISE response on the initial observed kinetics.

5. Observe the effects of varying soil moisture, soil type and temperature on exchange kinetics.

6. Model the exchange kinetics and develop predictive techniques for the estimation of soluble and exchangeable ion concentration using initial kinetics, and implement the technique into a proximal soil sensor.

8. Conclusions

This paper has presented a brief review of research using Ion Selective Electrode technology in proximal soil sensing. It has summarised some of the technical issues associated with the use of this technology for proximal soil sensing, and outlined the methods currently underway to quantify, minimise or solve these problems. Our preliminary results suggest that by characterizing the chemistry of the system and using a novel system design it may be possible to provide the response time, accuracy and robustness required for on-the-go proximal soil sensing.

9. References

Adamchuk, V. I., E. D. Lund, A. Dobermann and M. T. Morgan (2003). On-the-go mapping of soil properties using ion-selective electrodes. Stafford, J.V., Werner, A. (EEd.), Precision Agriculture. Wageningen Academic Publishers, Wageningen**:** 27-33.

Adamchuk, V. I., E. D. Lund, B. Sethuramasamyraja, M. T. Morgan, A. Dobermann and D. B. Marx (2005). Direct measurement of soil chemical properties on-the-go using ion-selective electrodes. Computers and Electronics in Agriculture. 48: 272-294.

Adamchuk, V. I., M. T. Morgan and S. M. Brouder (2006). Development of an on-the-go soil pH mapping method: Analysis of measurement variability. Applied Engineering in Agriculture. 22: 335-344.

Adamchuk, V. I., M. T. Morgan and D. R. Ess (1999). An automated sampling system for measuring soil pH. Transactions of the Asae. 42: 885-891.

Adsett, J. F., J. A. Thottan and K. J. Sibley (1999). Development of an automated on-the-go soil nitrate monitoring system. Applied Engineering in Agriculture. 15: 351-356.

Bergveld, P. (2003). Thirty years of ISFETOLOGY - What happened in the past 30 years and what may happen in the next 30 years. Sensors and Actuators B-Chemical. 88: 1-20.

Birrell, S. J. and J. W. Hummel (2001). Real-time multi ISFET/FIA soil analysis system with automatic sample extraction. Computers and Electronics in Agriculture. 32: 45-67.

Janata, J. (2004). Thirty years of CHEMFETs - A personal view. Electroanalysis. 16: 1831-1835.

Kim, H. J., J. W. Hummel, K. A. Sudduth and P. P. Motavalli (2007). Simultaneous analysis of soil macronutrients using ion-selective electrodes. Soil Science Society of America Journal. 71: 1867-1877.

Janata, J. (2004). Thirty years of CHEMFETs - A personal view. Electroanalysis. 16: 1831-1835. Kim, H. J., J. W. Hummel, K. A. Sudduth and P. P. Motavalli (2007). Simultaneous analysis of soil macronutrients using ion-selective electrodes. Soil Science Society of America Journal. 71: 1867-1877.

Lund, E.D., P.E. Colin, D. Christy, and P.E. Drummond (1999). Applying soil electrical conductivity technology to precision agriculture. p. 1089–1100. *In* P.C. Robert et al. (ed.) Precision agriculture. Proc. Int. Conf., 4th, St. Paul, MN. 19–22 July 1998. ASA, CSSA, and SSSA, Madison, WI.

Sethuramasamyraja, B., Adamchuk, V.I., Dobermann, A., Marx, D.B., Jones, D.D. and Meyer, G.E. (2008). Agitated soil measurement method for integrated on-the-go mapping of soil pH, potassium and nitrate contents. Computers and Electronics in Agriculture (in press).

Sudduth, K. A., S. T. Drummond, et al. (2001). Accuracy issues in electromagnetic induction sensing of soil electrical conductivity for precision agriculture. Computers and Electronics in Agriculture. 31: 239-264.

Viscarra Rossel, R. A. and A. B. McBratney (2003). Modelling the kinetics of buffer reactions for rapid field predictions of lime requirements. Geoderma. 114: 49-63.

Viscarra Rossel, R.A. and Walter, C. (2003). Rapid, quantitative and spatial field measurements of soil pH using an Ion Sensitive Field Effect Transistor. Geoderma, 119: 9-20

Viscarra Rossel, R.A., Thylén, L., McBratney, A.B. & Gilbertsson, M. (2004). Development of an on-the-go soil sensing system for determinations of soil pH and lime requirement. 7th International Conference on Precision Agriculture. July 25-28, Minneapolis MN, USA.